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(54)【発明の名称】　耐摩耗性に優れた高性能釣糸

(57)【要約】
【課題】　高強度・高弾性率を有しかつ耐摩耗性・耐久性に極めて優れる新規な高強度ポリエチレン繊維からなる高性能釣糸。
【解決手段】極限粘度[η]が５以上、その繰り返し単位が実質エチレンからなる高分子量ポリエチレンからなる分子配向繊維であって、前記繊維の平均強度が２２ｃＮ／ｄｔｅｘ以上であり、示差走査熱量計（ＤＳＣ）で求めた融解時の吸熱ピークが１４０～１４８℃に１つ以上存在し、かつ１４８℃以上に少なくとも１つ以上のピークを有する高強度ポリエチレン繊維、及び前記繊維のＪＩＳ　Ｂ法（ＪＩＳ　Ｌ１０９５）に準拠する方法により測定した磨耗試験において繊維の切断回数が１００，０００回以上である高強度ポリエチレン繊維を使用したことを特徴とする高性能釣糸。

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【特許請求の範囲】

【請求項１】極限粘度[η]が５以上、その繰り返し単位が実質エチレンからなる高分子量ポリエチレン分子配向繊維であって、前記繊維の平均強度が２２ｃＮ／ｄｔｅｘ以上であり、示差走査熱量計（ＤＳＣ）で求めた融解時の吸熱ピークが１４０～１４８℃に１つ以上存在し、かつ１４８℃以上に少なくとも１つ以上のピークを有するポリエチレン繊維からなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項２】ポリエチレン繊維が、示差走査熱量計（ＤＳＣ）測定における１４０から１４８℃に存在するピークの中で最大の吸熱量を有する第１融解ピーク（T_{m1}）と１４８℃以上にありかつ最大の吸熱量を有するる第２融解吸熱ピーク（T_{m2}）との高さの比が１．４：１．０～２．９：１．０であることを特徴とする請求項１記載の耐摩耗性に優れた高性能釣糸。

【請求項３】ポリエチレン繊維が、T_{m1}とT_{m2}との高さの比が１．５：１．０～２．９：１．０であることを特徴とする請求項１記載の耐摩耗性に優れた高性能釣糸。

【請求項４】請求項１記載のポリエチレン繊維を組紐にしてなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項５】請求項１記載のポリエチレン繊維を芯糸に配したカバーリングヤーンからなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項６】請求項１記載のポリエチレン繊維を撚糸にしてなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項７】極限粘度[η]が５以上、その繰り返し単位が実質エチレンからなる高分子量ポリエチレン分子配向繊維であって、前記繊維の平均強度が２２ｃＮ／ｄｔｅｘ以上であり、ＪＩＳ　Ｂ法（ＪＩＳ　Ｌ１０９５）に準拠して測定した摩耗試験において繊維の切断回数が１００，０００回以上であるポリエチレン繊維からなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項８】請求項７記載のポリエチレン繊維を組紐にしてなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項９】請求項７記載のポリエチレン繊維を芯糸に配したカバーリングヤーンからなることを特徴とする耐摩耗性に優れた高性能釣糸。

【請求項１０】請求項７記載の高強力ポリエチレン繊維を撚糸にしてなることを特徴とする耐摩耗性に優れた高性能釣糸。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、投げ釣りや深海釣りなど釣りの分野で要求される耐摩耗性を改善した釣糸に関するものである。

【０００２】

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【従来の技術】高強度ポリエチレン繊維に関しては例えば、特公昭６０－４７９２２号公報に開示されるごとく、超高分子量のポリエチレンを原料にし、いわゆる“ゲル紡糸法”により従来にない高強度・高弾性率繊維が得られることが知られており、既に産業上広く利用されている。今回発明した高強度ポリエチレン繊維による釣糸も極めて優れた高強度・高弾性率を有することは公知の通りだが、それら釣糸に対して近年はさらなる高性能の要求、特に釣糸の耐久性・耐疲労特性に対する要求が非常に高い。しかしながら、高強度ポリエチレン繊維による釣糸は確かに引張り強度・弾性率には優れるが、その反面、分子鎖が高度に配向した構造であることが災いして、耐久性、特に屈曲疲労性や耐摩耗性が、例えば通常の衣料用のポリエステルやナイロンに比べると劣るという問題点があった。かかる問題点は本釣糸を釣り具業界の多岐に渡る種々の分野でその応用を広げようとする場合の支障となっていた。

【０００３】

【発明が解決しようとする課題】かかる問題点を解消するためには分子鎖の配向程度をよりリラックスさせる必要があるがそのような方策は強度や弾性率を低下させる方向であり採用することができない。またポリエチレン繊維は分子鎖間に強い相互作用を持たず、繰り返しの疲労にはたやすくフィブリル化を起こすことも、その繊維の耐久性を向上させることを非常に困難にしていた。以上より、強度を維持したまま、あるいはさらに強度・弾性率を向上せしめて、かつ高度の屈曲疲労特性あるいは摩耗特性を有する高強度ポリエチレン繊維による釣糸を得る事が課題である。

【０００４】

【課題を解決するための手段】本発明者らは、前記目的を達成すべく鋭意検討を重ねた結果、本発明を得るに至った。即ち本発明は、極限粘度[η]が５以上、その繰り返し単位が実質エチレンからなる高分子量ポリエチレン分子配向繊維であって、前記繊維の平均強度が２２ｃＮ／ｄｔｅｘ以上であり、示差走査熱量計（ＤＳＣ）で求めた融解時の吸熱ピークが１４０～１４８℃に１つ以上存在し、かつ１４８℃以上に少なくとも１つ以上のピークを有するポリエチレン繊維からなることを特徴とする耐摩耗性に優れた高性能釣糸、ポリエチレン繊維が、示差走査熱量計（ＤＳＣ）測定における１４０から１４８℃に存在するピークの中で最大の吸熱量を有する第１融解ピーク（T_{m1}）と１４８℃以上にありかつ最大の吸熱量を有するる第２融解吸熱ピーク（T_{m2}）との高さの比が１．４：１．０～２．９：１．０であることを特徴とする上記記載の耐摩耗性に優れた高性能釣糸、ポリエチレン繊維が、T_{m1}とT_{m2}との高さの比が１．５：１．０～２．９：１．０であることを特徴とする上記記載の耐摩耗性に優れた高性能釣糸、

【０００５】上記記載のポリエチレン繊維を組紐にして

なることを特徴とする耐摩耗性に優れた高性能釣糸、上記記載のポリエチレン繊維を芯糸に配したカバーリングヤーンからなることを特徴とする耐摩耗性に優れた高性能釣糸、及び上記記載のポリエチレン繊維を撚糸にしてなることを特徴とする耐摩耗性に優れた高性能釣糸である。

【０００６】また極限粘度[η]が５以上、その繰り返し単位が実質エチレンからなる高分子量ポリエチレン分子配向繊維であって、前記繊維の平均強度が２２ｃＮ／ｄｔｅｘ以上であり、ＪＩＳ　Ｂ法（ＪＩＳ　Ｌ１０９５）に準拠して測定した摩耗試験において繊維の切断回数が１００，０００回以上であるポリエチレン繊維からなることを特徴とする耐摩耗性に優れた高性能釣糸、上記記載のポリエチレン繊維を組紐にしてなることを特徴とする耐摩耗性に優れた高性能釣糸、上記記載のポリエチレン繊維を芯糸に配したカバーリングヤーンからなることを特徴とする耐摩耗性に優れた高性能釣糸及び、上記記載の高強力ポリエチレン繊維を撚糸にしてなることを特徴とする耐摩耗性に優れた高性能釣糸である。

【０００７】本発明における高強度ポリエチレン繊維の極限粘度[η]は５以上であることが肝要である。５未満では力学的特性、特に引張り強度を発現するのに十分でなく本発明の目的とする高強度繊維を得る事が極めて困難となる。極限粘度の上限は特に無いが製糸上の安定性や生産速度の観点さらには得られる繊維の耐疲労性の観点からは２．９以下であることが好ましい。２．９を越えると紡出糸の延伸条件によっては耐疲労特性が反って劣る場合も起こり得る。

【０００８】また、本発明である高性能釣糸に使用される高強度ポリエチレン繊維は、その原料とするポリマーについてはその最終の繊維の極限粘度を満足するものであれば、特に制限するものでは無いが、耐疲労性を極限まで高める目的においてはより分子量分布の狭い原料を用いるのが好ましく、メタロセン系触媒等の重合触媒を用いることで得られる分子量分布指数Ｍｗ／Ｍｎが５以下のものを使用する事はさらに好ましい。

【０００９】本発明である高性能釣糸に使用される高強度ポリエチレン繊維における最も重要な構成はその繊維の示差走査熱量計（ＤＳＣ）で求めた融解時の吸熱ピークが１４０～１４８℃に少なくとも１つ以上存在し、かつ１４８℃以上に少なくとも１つ以上のピークを有することである。例えば特開昭６３－２７５７０８号公報にはエチレン以外のαオレフィンを共重合するという特殊な手法により得られた高強度ポリエチレン繊維において、その繊維をアルミパーン等に巻き付けて、繊維が緊張状態になるようにＤＳＣ測定した場合に主ピークに加えて共重合に由来する複数の高温ピークが観察されるという技術開示があるが、通常そのような高強度ポリエチレン繊維を、繊維が緊張拘束された状態でＤＳＣ測定すると融点の上昇や、場合によっては結晶転移等による複数のピークが発生することは良く知られている。

【００１０】本発明である高性能釣糸に使用される高強度ポリエチレン繊維は、実質エチレン単位の実質ホモポリマーに近い高強度ポリエチレン繊維であり、かつ後に述べる本発明のＤＳＣの測定手法において、繊維を一旦５ｍｍ以下に切断し完全に無拘束の状態で測定している。この様な場合においても、かかる高温に複数の融解ピークを有する高強度ポリエチレン繊維は、発明者の知るところ新規な知見である。このように完全な無拘束の状態でも高温域に複数の融解ピークが存在する理由として、通常のポリエチレン結晶（以下「ＥＣ」という）とは異なる高温融解タイプの結晶構造（以下「ＨＭＣ」という）が存在していると推定される。後に実施例で示す通り、繊維の表面での含有溶剤をより積極的に除去し構造形成させると好ましい結果が得られることから、そのＨＭＣは繊維の表面層に優先的に配置されていると考えられ、このＨＭＣ層が繊維の強度を維持する機能を有し、極めて優れた耐疲労特性あるいは摩耗特性を発生させる要因であると推定することが可能である。

【００１１】特開平６１－２８９１１１号公報には特殊な溶剤を２種類用いた紡糸方法により得られた半延伸糸が、言うところの無拘束状態で測定して複数の融点ピークを観察された実施例が開示されている。かかる実施例の最終的な延伸糸の融解ピークがいかなるものか想像するしかない。また、この半延伸糸の言うところの無拘束状態がいかなる状態かも推測するしかないが、通常糸を細く切断しないで、測定用のアルミパーンに挿入して測定するだけでは、例えその繊維がアルミ小片に巻き付けた通常の測定に比べて拘束状態が少ないと言えども、実際にはパーン中の糸はパーン底部と蓋との間で局所的に固定されたり、試料全般に応力の不均一分布が生じることによりしばしば多重のピークが観測されるのは常であり公知の現象である。このような測定上の影響を避けるために、本発明者らが行うように慎重に非常に短い長さに切断する必要がある。仮に該公報が本発明と同一の測定であるとしても、実施例に記載の温度域は本特許で規定する範囲外にあり、発明の目指す耐疲労性や屈曲摩耗特性に劣るであろうことことが以下に述べる事情により推測される。元より、公報に開示されている方法、すなわち紡糸直後に第１溶剤が第２溶剤に実質に抽出される緩慢な手法では表面層に緻密な構造を取ることは困難である。

【００１２】本発明である高性能釣糸に使用される高強度ポリエチレン繊維においては、ＤＳＣにより求めた融解ピークが１４０℃～１４８℃に少なくとも１つ以上存在する必要がある。特にそれは複数のピークにおいて最も吸熱値の大きな主ピークであることが好ましい。主ピークは繊維の主要部分を占める平均構造（ＥＣ）を反映すると考えられ、それが１４０℃未満では繊維自体の耐熱性が十分でなくなる。またそれが１４８℃を越える

と、平均の繊維構造がむしろ拘束力の高い例えば伸び切り鎖構造的になり、繊維自体の疲労性はむしろ低下する。本発明者らは、繊維の疲労特性、特にこの場合は屈曲疲労特性がこの主ピークが１４０℃～１４８℃にある場合最適になることを見出し本発明である高性能ポリエチレンに使用する繊維を得るに到達した。

【００１３】一方、本発明である高性能釣糸に使用される高強度ポリエチレン繊維は１４８℃以上に少なくとも一つのピークの存在が必要である。即ち、本発明に係る繊維のＤＳＣ測定における複数の吸熱ピークにおいて１４８℃以上に存在する第２融解ピーク（T_{m2}）が耐疲労性特性、特に本発明において重要な耐摩耗特性に大きく影響するHMC構造と対応すると考えている。その形成のメカニズムは後程記述するが、１４８℃以上にピークを有しない繊維は耐摩耗特性が極端に悪くなる。

【００１４】このように、本発明である高性能釣糸に使用される高強度ポリエチレン繊維の疲労特性、特に耐磨耗特性は従来の高強度ポリエチレン繊維と比較して格段に改善されたものとなる。具体的には、ＪＩＳ　Ｂ法（ＪＩＳ　Ｌ１０９５）に準拠して測定した磨耗試験において繊維の切断回数が１００，０００回以上の高強度ポリエチレン繊維となる。

【００１５】本発明である高性能釣糸に使用される高強度ポリエチレン繊維を製造する方法は、慎重でかつ新規な製造法を採用する必要があり以下に開示する方法を推奨するがもちろんそれに限定されるものではない。即ち、当該繊維の製造に当たっては、その原料となる高分子量のポリエチレンの極限粘度[η]は５以上であることが肝要であり、好ましくは８以上、さらに好ましくは１０以上である。極限粘度が５未満であると、本来所望とする繊維の平均強度が２２ｃＮ／ｄｔｅｘ以上の高強度繊維が得られない。一方、上記の如く極限粘度に上限は無いが、耐疲労特性付与の観点からは原料となるポリマーの極限粘度は２．９以下が好ましい。

【００１６】本発明である高性能釣糸に使用される高強度ポリエチレン繊維においてはポリマーの主成分はエチレン成分が９９．５ｍｏｌ％以上、好ましくは９９．８ｍｏｌ％以上の実質的にポリエチレンのホモポリマーであることが重要である。重合の副反応や重合速度を向上せしめる、あるいは得られる繊維のクリープ特性等を改善する目的で極く少量の分岐の導入はむしろ推奨されるが、αオレフィン等の共重合成分が増えすぎると、繊維の疲労特性には好ましくない。この原因は定かではないが少量のαオレフィンを共重合すると結晶内での分子鎖間の滑りが抑制され、これが連続的な繰り返しの変形に対して応力を緩和させる（逃がす）作用を抑制するのではないかと推定している。

【００１７】本発明である高性能釣糸に使用される高強度ポリエチレン繊維の推奨する製造方法においては、このような高分子量のポリエチレンをデカリン・テトラリン等の揮発性の溶剤やパラフィン、固体パラフィン等の不揮発性の溶剤を用いて均一な溶解を行い紡糸用のドープを得ることができる。この際、濃度は５０％以下、好ましくは２．９％以下が好ましい。さらに言えば使用される溶液は揮発性の溶媒であることが好ましい。常温固体または非揮発性の溶剤では、溶剤を糸中から抽出する速度が緩慢であり、本発明で述べるHMCの形成を十分に行う事が困難である。この理由は、揮発溶媒を用いることで、紡糸の段階において、表面の溶媒がより積極的に蒸発し、繊維表面近傍に濃度の高くかつ分子鎖がより配向しかつ分子鎖同士が連結したような特異な結晶構造（HMC）を形成することが可能となると推定される。従来の紡糸技術の常識においてはこのような表面と内部の構造差は繊維の強度を低下させる要因となり、できるだけ断面方向の均一にするべく紡糸条件を選択することが、ゲル紡糸に限らずポリビニルアルコールやポリアクリルニトリルなどの乾式紡糸・湿式紡糸はもとより溶融紡糸においても、つまり紡糸全般に携わる当該技術者の常識であった。

【００１８】本発明者らはこの常識に反して、紡糸の段階でむしろ積極的に内層と外層の構造を変化せしめ、具体的には表面層の溶剤を瞬間的に積極的に排除し、それにより表面層に紡糸張力を集中せしめることでHMC層を形成することにより、強度・弾性率を維持しつつも、極めて優れた耐摩耗特性・屈曲疲労特性を具備する繊維が得られうることを見出し本発明に到達した。

【００１９】即ち前述のように、本発明である高性能釣糸に使用される高強度ポリエチレン繊維に係る繊維のＤＳＣ測定における複数の吸熱ピークにおいて１４８℃以上に存在する第２融解ピーク（T_{m2}）が少なくともこのHMCに由来するものと考えている。具体的には、この第２融解ピークの量をコントロールすることで最適な耐疲労特性を有する高強度ポリエチレンを提供可能であることを見出して上記仮説に到達した。

【００２０】かかる表面層に存在するHMCはお互いの分子がより交絡しフィブリル化しにくい構造を有している事が想像される。即ち、高強度ポリエチレン繊維を代表とする配向繊維の屈曲や摩耗による疲労の第一の原因は繊維の表面層からのフィブリル化にあることは一般に知られる事実である。より緻密な表面構造を有する本発明の繊維が耐屈曲疲労特性や耐摩耗特性に優れるのはこのような事情によると推定している。

【００２１】しかしながら、かかるHMCにおいて重要であるのはその全体の結晶構造に占める割合である。すなわち前述のごとく、１４０℃～１４８℃の存在する第１吸熱ピーク（T_{m1}）がＥＣの融解に由来し、１４８℃以上に存在する第２のピーク（T_{m2}）が少なくともHMCに由来すると推定しているが、各温度域における最大の吸熱ピークの高さの比が１．５：１．０～２．９：１．０、好ましくは２．０：１．０～２．９：１．０、

更に好ましくは２．１：１．０～２．８：１．０であることは重要である。１．５：１．０より低温側のピークが相対的に低くなるとこれは繊維の表面層を形成すると推定されるＨＭＣの分率が大きくなりすぎる事を意味し、耐疲労特性はむしろ悪化する。これは表面層が過度に硬化することで坐屈疲労のような劣化が促進されるためと推定される。一方、その比が２．９：１．０よりも高温側のピーク値が小さくなる、ＨＭＣ鎖が相対的に少なくなり強度特性等に支障はないが本発明の目的とする耐疲労特性の改良された高強度ポリエチレン繊維の素材性能を効率よく反映させた高性能釣糸を満足することができない。

【００２２】いずれにしても本発明によって得られる高性能釣糸は、従来と同程度以上の強度・弾性率を有して尚、耐屈曲・摩耗疲労特性に優れると共に、原理は推定でしかないが、表面層がより緻密であることを特徴として耐刃性、耐切創性に優れる高強度ポリエチレン繊維を使用することで機能面、実用面で画期的な高性能釣糸を得ることを可能をするものである。

【００２３】本高性能釣糸の原材料として使用される高強度ポリエチレン繊維を製造する際に推奨される手法は、紡糸での口金直下で出てきた吐出溶液に対して強制的に高温の不活性ガスを供給し、糸条の表面の溶剤を積極的に蒸発させることである。これにより、表面に極く薄いＨＭＣ層を形成させ、紡糸での張力を集中させることで上記概念の分子鎖がお互いに連結した特異な構造を出現させることができる。この際の不活性ガスの温度は６０℃以上、好ましくは８０℃以上、さらに好ましくは１００℃以上１５０℃未満であることが推奨される。この際、ガスは経済的な観点から窒素ガスを用いることが推奨されるが限定されるものでは無い。

【００２４】この様にして得られた繊維は、再度加熱されて残留溶剤を蒸発せしめながら数倍に延伸を行い、場合によって多段階延伸を行っても良い。紡糸で一旦形成された表面のＨＭＣ構造が後段の延伸では消失することなく、前述の極めて優れた特性を有する新規な繊維を得る事ができる。

【００２５】本発明による釣糸の形態は特に問わないが、上記高強度ポリエチレン繊維を組紐したもの、該繊維を芯糸に配したカバーリングヤーンしたもの、或いは該繊維を撚糸にしたものが推奨できる。

【００２６】以下に本発明における本高性能釣糸を構成する高強度ポリエチレン繊維の特性値に関する測定法および測定条件を説明する。

【００２７】（強度・弾性率）本発明における強度，弾性率は、オリエンティック社製「テンシロン」を用い、試料長２００ｍｍ（チャック間長さ）、伸長速度１００％／分の条件で歪一応力曲線を雰囲気温度２０℃、相対湿度６５％条件下で測定し、曲線の破断点での応力を強度（ｃＮ／ｄｔｅｘ）、曲線の原点付近の最大勾配を与える接線より弾性率（ｃＮ／ｄｔｅｘ）を計算して求めた。なお、各値は１０回の測定値の平均値を使用した。

【００２８】（極限粘度）１３５℃のデカリンにてウベローデ型毛細粘度管により、種々の希薄溶液の比粘度を測定し、その粘度の濃度に対するプロットの最小２乗近似で得られる直線の原点への内挿点より極限粘度を決定した。測定に際し、サンプルを約５ｍｍ長の長さにサンプルを分割または切断し、ポリマーに対して１ｗｔ％の酸化防止剤（商標名「ヨシノックスＢＨＴ」吉富製薬製）を添加し、１３５℃で４時間攪拌溶解して測定溶液を調整した。

【００２９】（示差走査熱量計測定）示差走査熱量計測定はパーキンエルマー社製「ＤＳＣ７」を用いた。予め５ｍｍ以下に裁断したサンプル(繊維)をアルミパンに約５ｍｇ充填封入し、同様の空のアルミパンをリファレンスにして１０℃／分の昇温速度で不活性ガス下、室温から２００℃まで上昇させ、その吸熱ピークを求めた。得られた曲線のベースライン補正をし、１４０℃以上の融解ピークの数をカウントし、また１４０℃～１４８℃の範囲で最も吸熱量の大きいピークを第１融解ピークとし、１４８℃以上にあり最も吸熱量の大きいピークを第２融解ピークとし、それぞれの温度およびピーク高さを求め、後者で前者を除することでピーク比率を求めた。尚、ピークがショルダー状で判別しにくい場合は１５０℃における吸収の高さを第２融解ピークとして代用してピーク比を算出した。

【００３０】（糸の耐摩耗性試験）本釣糸の耐摩耗特性は、繊維をなるべく１５００ｄｔｅｘ相当になるように合糸あるいは調整し、ＪＩＳ　Ｂ法（ＪＩＳ　Ｌ１０９５）に準拠する方法により測定した。尚、摩擦子は０．９ｍｍΦの硬質鋼を用い、荷重は０．５ｇ／ｄ、速度１１５回／分、往復距離２．５ｃｍ、角度１１０度で実施しｎ＝２回の平均値の１０００回未満の位は四捨五入して採用した。

【００３１】本発明による釣糸の耐摩耗特性は、本発明による高強度ポリエチレン繊維を組紐に調整したものを次の試験方法にて行った。

【００３２】試験機はシートベルトの六角棒摩耗試験機を改良して、六角棒の位置にセラミックガイゴを配置して試験機とした。よってストローク長、角度等に関しては、ＪＩＳ－Ｄ－４６０４（１９９５）に準じている。図２に示すように、セラミックガイドにサンプルを通し、一方をドラムに固定し他方に荷重をかける。荷重は芯糸のデニール値に対し、１ｇ／ｄの比率で荷重をかける。１０００回ドラムを往復運動させた後に、サンプルの状態を目視判定した。耐摩耗試験の評価として全く変化がなければ○、少し毛羽立てば△、毛羽立ちが激しいもしくは一部でも切断すれば×と評価した。

【００３３】（強度保持率）強力測定法はＪＩＳ Ｌ １０１３に準じていて、上項で述べた耐摩耗性試験前後の

試料で強力保持率を比較した。

【００３４】以下、実施例をもって本発明を具体的に説明するが、本発明はこれらに限定されるものではない。

【００３５】

【実施例】以下、実施例をもって本発明を説明する。

（実施例１）極限粘度が２１．０、分子量分布指数Ｍｗ／Ｍｎ＝３．７の超高分子量ポリエチレンのホモポリマーを１０ｗｔ％およびデカヒドロナフタレン９０ｗｔ％のスラリー状の混合物を分散しながら２３０℃の温度に設定したスクリュー型の混練り機で溶解し、１７０℃に設定した直径０．７ｍｍを４００ホール有する口金に軽量ポンプにて単孔吐出量１．４ｇ／ｍｉｎで供給した。ノズル直下に設置したスリット状の気体供給オリフィスにて１．２m/秒の高速度で１００℃に調整した窒素ガスをできるだけ糸条に均等に当たるようにして繊維の表面のデカリンを積極的に蒸発させ、その直後３０℃に設定された空気流にて実質的に冷却し、ノズル下流に設置されたネルソン状のローラーにて７５ｍ／分の速度で引き取られた、この際に糸状に含有される溶剤は元の重量の約半分まで低下していた。引き続き、得られた繊維を１００℃の加熱オーブン下で４倍に延伸した、引き続きこの繊維を１４９℃に設置した加熱オーブン中にて４倍で延伸した。途中破断することなく均一な繊維を得る事ができた、トータルの繊維の繊度は４５５ｄｔｅｘであった。得られた繊維の物性値を表１に示す。次ぎに得られた繊維を用いて５５．６ｄｔｅｘ×４本の組紐に調整してなる釣糸を作成し、摩耗試験に供した。その結果を表２に示す。

【００３６】（実施例２）実施例１における高温加熱流の温度を１２０℃、平均風速を１．４ｍ／秒とした他は同様の操作で紡糸を行った、若干耐久性に低下が見られるが満足の行く値であった。次ぎに得られた繊維を用いて１１１．１ｄｔｅｘ×４本の組紐にしたものを作成し、磨耗試験に供した。その結果を表２に示す。

【００３７】（実施例３）実施例１における主成分ポリマーとして極限粘度が１２．１、分子量分布指数Ｍｗ／Ｍｎ＝５．４のポリマーを用い、溶液の粘度を３０％にした他は、同様の操作で紡糸を実施した。１段延伸は３倍の延伸が可能であった、２段目の延伸では２．２倍が限度であった。表１にその結果を示す。全体の繊度は１１６０ｄｔｅｘであった。強度が若干低下した。次ぎに得られた繊維を用いて１１１．１ｄｅｘ×４本の組紐にしたものを作成し、磨耗試験に供した。その結果を表２に示す。

【００３８】（実施例４）実施例１の高強力ポリエチレンからなる繊維を芯糸（８８０ｄｔｅｘ）及び巻き糸（２２０ｄｔｅｘ）にしたカバーリング糸を作成し、表２の摩耗性試験を行い磨耗試験に供した。その結果を表２に示す。

【００３９】（実施例５）実施例１の高強力ポリエチレンからなる繊維（１３２０ｄｔｅｘ）を撚糸（撚数１００ｔ／ｍ）としたものを作成し、表２の摩耗性試験を行い磨耗試験に供した。その結果を表２に示す。

【００４０】（比較例１）実施例１の実験において、ノズル直下での気体スリットでの熱風の付与を止め、直ちに３０℃の窒素ガスにて冷却を実施した。紡糸は７５m/分で延伸倍率も２段階目が若干低下し低い倍率しか得られなかったすなわち、１段延伸が４．０倍、２段延伸が３．５倍であった。得られた繊維の物性を表１に示す。また図４にＤＳＣ結果を示す。強度・弾性率的には実施例１にほぼ匹敵する繊維が得られたが、耐摩耗性に劣り、熱的な性質も満足しなかった、すなわち高温側のピークがショルダー的になり明確なピークが得られなかった。１４０℃～１４８℃にもピークは得られなかたが、１４５．５℃のピーク値と１５０℃での吸熱量とをそれぞれ第１吸熱、第２吸熱ピークに代替し、その比率を参考までに算出した。次ぎに得られた繊維を用いて５５．６ｄｔｅｘ×４本の組紐に調整したものを作成し、磨耗試験に供した。その結果を表２に示す。

【００４１】（比較例２）実施例１のポリマーを流動パラフィンで溶解した後は同様の操作および紡糸条件で未延伸の紡出糸を得た。ただし、紡糸のＮｚ下に配置した約８０℃に設定したn-デカンのバス中で溶剤を実質抽出しながら４倍の延伸を行った。エアーギャプにおける積極的な気体による冷却は実施しなかった。得られたｎ－デカンを含む半延伸糸を高温の不活性ガスのオーブン中１４８℃にて４倍延伸して第２溶剤を実質乾燥させて延伸糸を得た。繊維の物性を表１に示す。強度・弾性率的には今回も実施例１にほぼ匹敵する繊維が得られたが、ＤＳＣは完全にシングルピークでありむしろ１３３℃付近に小さいショルダーが観察された。得られた繊維の耐摩耗特性は非常に低レベルであった。次ぎに得られた繊維を用いて５５．６ｄｔｅｘ×４本の組紐に調整したものを作成し、磨耗試験に供した。その結果を表２に示す。

【００４２】

【表１】

11　　12

実験	[η] (g/dl)	繊度 (dtex)	強度 (cN/dtex)	弾性率 (cN/dtex)	摩耗試験回数	融解ピークの数	第１吸熱ピーク温度	第２吸熱ピーク温度	ピークの高さの比
実施例１	１８．５	４５５	３８．１	１５２１	421,000	３	１４２．０	１４８．５	２．４：１
実施例２	１８．４	４４８	３５．２	１６１２	356,000	２	１４４．７	１５１．３	２．４：１
実施例４	９．４	１１５０	２８．５	１０５５	381,000	２	１４４．３	１５１．７	２．０：１
比較例１	１８．４	５４１	３４．２	１５１６	98,000	２	１４５．５	明確で無い	（３．２：１）
比較例２	１８．３	４７１	３５．７	１６２３	57,000	１	１４５．５	観測できず	—

【００４３】　　＊　＊【表２】

実験	繊度 (dtex)	強度 (cN/dtex)	破断強力 (kg)	弾性率 (cN/dtex)	摩耗試験	
					１０００回	強力保持率(%)
実施例１	２２２．６	２３．８	４．９	５９４．７	形状変化なし	８９．８
実施例２	５０３．４	２３．３	９．５	５８３．２	形状変化なし	９０．２
実施例３	５５０．１	２６．８	１２．９：	５９９．７	形状変化なし	８４．５
実施例４	１１１０．１	２５．４	２４．９	４０９．８	形状変化なし	８２．９
実施例５	１４５０．２	２８．５	３８．７	９４５．３	形状変化なし	８０．６

【００４４】
【発明の効果】高強度・高弾性率を有しかつ、衣料糸用汎用繊維に匹敵するあるいは優れた耐摩耗・疲労特性に優れる新規な高強度ポリエチレン使用による高性能釣糸を提供することを可能とした。

CLAIMS

[Claim(s)]

[Claim 1]Limiting viscosity [eta] is the amount polyethylene molecule orientation textiles of Polymer Division which 5 or more and its repeating unit become from real ethylene, One or more endothermic peaks at the time of fusion which mean intensity of said textiles is 22 or more cN/dtex, and was calculated with a differential scanning calorimeter (DSC) exist in 140-148 **, And a highly efficient fishing line excellent in abrasion resistance becoming not less than 148 ** from a polyethylene fiber which has at least one or more peaks.

[Claim 2]A polyethylene fiber, A differential scanning calorimeter. (DSC) A ratio of height with the 2nd fusion endothermic peak (T_{m2}) of ** which is in the 1st melting peak (T_{m1}) that has the maximum amount of endothermics in a peak which exists in 140 in measurement to 148 **, and not less than 148 **, and has the maximum amount of endothermics 1.4:. A highly efficient fishing line excellent in the abrasion resistance according to claim 1 being 1.0 to 2.9:1.0.

[Claim 3]A highly efficient fishing line which excelled [polyethylene fiber] in the abrasion resistance according to claim 1, wherein a ratio of height of T_{m1} and T_{m2} is 1.5:1.0 to 2.9:1.0.

[Claim 4]A highly efficient fishing line which used the polyethylene fiber according to claim 1 as a braid, and was excellent in abrasion resistance characterized by things.

[Claim 5]A highly efficient fishing line excellent in abrasion resistance consisting of covering yarn which allotted the polyethylene fiber according to claim 1 to wadding.

[Claim 6]A highly efficient fishing line which made throwing the polyethylene fiber according to claim 1, and was excellent in abrasion resistance characterized by things.

[Claim 7]Limiting viscosity [eta] is the amount polyethylene molecule orientation textiles of Polymer Division which 5 or more and its repeating unit become from real ethylene, A highly efficient fishing line whose mean intensity of said textiles is 22 or more cN/dtex and which was excellent in abrasion resistance, wherein the number of times of cutting of textiles consists of a polyethylene fiber which is 100,000 times or more in a wear test measured based on the JIS B method (JIS L1095).
[Claim 8]A highly efficient fishing line which used the polyethylene fiber according to claim 7 as a braid, and was excellent in abrasion resistance characterized by things.
[Claim 9]A highly efficient fishing line excellent in abrasion resistance consisting of covering yarn which allotted the polyethylene fiber according to claim 7 to wadding.
[Claim 10]A highly efficient fishing line which made throwing the high strength polyethylene fiber according to claim 7, and was excellent in abrasion resistance characterized by things.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]this invention -- surf-fishing and deep sea -- it is related with the fishing line which has improved the abrasion resistance demanded in the field of fishing, such as fishing.
[0002]
[Description of the Prior Art]Polyethylene of ultrahigh molecular weight is used as a raw material, it is known by what is called a "gel spinning method" that the high intensity and the rate textiles of high elasticity which are not in the former will be obtained, and it is widely used already industrially so that it may be indicated by JP,S60-47922,B, concerning a high intensity polyethylene fiber. Having the high intensity and the rate of high elasticity which was extremely excellent also in the fishing line by the high intensity polyethylene fiber invented this time has [publicly known passage] the further highly efficient demand, especially a dramatically high demand of as opposed to the endurance and the fatigue characteristics-proof of a fishing line to these fishing lines but in recent years. However, although surely the fishing line by a high intensity polyethylene fiber is excellent in tensile strength and an elastic modulus, On the other hand, it suffered misfortune that it is the structure in which the chain carried out orientation highly, and there was a problem that endurance especially bending fatigue nature, and abrasion resistance were inferior

compared with usual polyester and nylon for garments, for example. This problem had become the trouble in the case of extending the application in various fields to which the fishing tackle industry crosses this fishing line variably.

[0003]

[Problem(s) to be Solved by the Invention]In order to cancel this problem, it is necessary to make the orientation grade of a chain relax more but, and such a policy is a direction in which intensity and an elastic modulus are reduced, and cannot be adopted. The polyethylene fiber did not have a strong interaction between chains, but it was also made very difficult that causing fibrillation easily for repeated fatigue raised the endurance of the textiles. As mentioned above, it is SUBJECT to obtain the fishing line by the high intensity polyethylene fiber which intensity and an elastic modulus are made to improve further, and has the advanced bending fatigue characteristic or abrasion characteristic, with intensity maintained.

[0004]

[Means for Solving the Problem]This invention persons came to get this invention, as a result of repeating examination wholeheartedly that said purpose should be attained. Namely, limiting viscosity [eta] of this invention is the amount polyethylene molecule orientation textiles of Polymer Division which 5 or more and its repeating unit become from real ethylene, One or more endothermic peaks at the time of fusion which mean intensity of said textiles is 22 or more cN/dtex, and was calculated with a differential scanning calorimeter (DSC) exist in 140–148 **, And a highly efficient fishing line excellent in abrasion resistance becoming not less than 148 ** from a polyethylene fiber which has at least one or more peaks, A polyethylene fiber, A differential scanning calorimeter. (DSC) A ratio of height with the 2nd fusion endothermic peak (T_{m2}) of ** which is in the 1st melting peak (T_{m1}) that has the maximum amount of endothermics in a peak which exists in 140 in measurement to 148 **, and not less than 148 **, and has the maximum amount of endothermics 1.4:. A highly efficient fishing line which was excellent in the abrasion resistance of the above–mentioned description by which it is characterized in a ratio of height of T_{m1} and T_{m2} being the highly efficient fishing line which was excellent in the abrasion resistance of the above–mentioned description by which it is characterized in it being 1.0 to 2.9:1.0, and a polyethylene fiber being 1.5:1.0 to 2.9:1.0, [0005]A highly efficient fishing line which used a polyethylene fiber of the above–mentioned description as a braid, and was excellent in abrasion resistance characterized by things, They are a highly efficient fishing line excellent in abrasion resistance consisting of covering yarn which allotted a polyethylene fiber of the above–mentioned description to wadding, and the highly

efficient fishing line which made a polyethylene fiber of the above-mentioned description throwing, and was excellent in abrasion resistance characterized by things.
[0006]Limiting viscosity [eta] is the amount polyethylene molecule orientation textiles of Polymer Division which 5 or more and its repeating unit become from real ethylene, A highly efficient fishing line whose mean intensity of said textiles is 22 or more cN/dtex and which was excellent in abrasion resistance, wherein the number of times of cutting of textiles consists of a polyethylene fiber which is 100,000 times or more in a wear test measured based on the JIS B method (JIS L1095), A highly efficient fishing line which used a polyethylene fiber of the above-mentioned description as a braid, and was excellent in abrasion resistance characterized by things, They are a highly efficient fishing line excellent in abrasion resistance consisting of covering yarn which allotted a polyethylene fiber of the above-mentioned description to wadding, and the highly efficient fishing line which made throwing a high strength polyethylene fiber of the above-mentioned description, and was excellent in abrasion resistance characterized by things.
[0007]As for limiting viscosity [eta] of a high intensity polyethylene fiber in this invention, it is important that it is five or more. Less than five are not enough to reveal kinetic property, especially tensile strength, and it becomes very difficult to obtain high intensity textiles made into the purpose of this invention. Although there is no maximum in particular of limiting viscosity, from stability on silk manufacture, a viewpoint of a production rate, and also a fatigue-resistant viewpoint of textiles obtained, it is preferred that it is 2.9 or less. It may happen, also when 2.9 is exceeded, and fatigue characteristics-proof curve and are inferior depending on extension conditions of spinning thread.
[0008]A high intensity polyethylene fiber used for a highly efficient fishing line which is this invention, If limiting viscosity of the last textiles is satisfied about polymer used as the raw material, Although it does not restrict in particular, it is preferred to use a raw material with narrower molecular weight distribution in the purpose of improving fatigue resistance to a limit, and it is still more preferred that molecular-weight-distribution index Mw/Mn obtained by using polymerization catalysts, such as a metallocene system catalyst, uses five or less thing.
[0009]At least one or more endothermic peaks at the time of fusion which asked for the most important composition in a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention with a differential scanning calorimeter (DSC) of the textiles exist in 140-148 **, And it is having at least one or more peaks at not less than 148 **. For example, in a high intensity polyethylene fiber obtained by

a special technique of carrying out copolymerization of the alpha olefins other than ethylene to JP,S63-275708,A, Twist the textiles around aluminum PAN etc., when DSC measurement is carried out so that textiles may be in turgescence, disclosure of technology that two or more elevated-temperature peaks which originate in copolymerization in addition to a main peak are observed occurs, but. Usually, if textiles carry out DSC measurement of such a high intensity polyethylene fiber where a stress restraint is carried out, it is known well that a rise of the melting point and two or more peaks depended on crystal transition etc. depending on the case will occur.

[0010]A high intensity polyethylene fiber used for a highly efficient fishing line which is this invention is a high intensity polyethylene fiber near a real homopolymer of a real ethylene unit, and in the measurement technique of DSC of this invention described later, textiles were once cut to 5 mm or less, and it has measured them in the state of no restraining thoroughly. Also in this case, a high intensity polyethylene fiber which has two or more melting peaks to this elevated temperature is new knowledge a place which an artificer gets to know. Thus, even a state where perfect it does not restrain is presumed that a crystal structure (henceforth "HMC") different elevated-temperature fusion type from the usual polyethylene crystal (henceforth "EC") as a Reason two or more melting peaks exist in a pyrosphere exists. From a desirable result being obtained, if a content solvent in the surface of textiles is removed more positively and structure formation is carried out as working example shows later. It is possible to presume that it is a factor which generates fatigue characteristics-proof or an abrasion characteristic which is considered that that HMC is arranged with the priority to a surface layer of textiles, has a function in which this HMC layer maintains intensity of textiles, and was extremely excellent.

[0011]Working example which a half-full oriented yarn obtained by JP,H61-289111,A with a spinning method using a special solvent two kinds measured [working example] by an unrestrained condition to say, and had two or more melting point peaks observed is indicated. A melting peak of a final full oriented yarn of this working example cannot but imagine in what kind of thing. Only by inserting in aluminum PAN for measurement and measuring without usually cutting thread thinly although an unrestrained condition which this half-full oriented yarn says cannot but guess [whether it is also in what kind of state, or], Also although it says that there are few restrained conditions compared with the usual measurement which was compared and the textiles twisted around an aluminum wafer, When thread in Pan is locally fixed between the Pan pars basilaris ossis occipitalis and a lid actually or inhomogeneous

distribution of stress arises in a sample at large, it is a usual state that a multiplex peak is often observed, and it is a publicly known phenomenon. In order to avoid influence of [on such measurement], it is necessary to cut to prudent very short length so that this invention persons may carry out. even if this gazette is the same measurement as this invention, a temperature region given in working example will be out of a range specified by this patent, and will be inferior to fatigue resistance and a crookedness abrasion characteristic which an invention aims at -- I will come out -- things -- things are guessed by a situation described below. It is more difficult than a dimension to take a structure precise to a surface layer by a method currently indicated by gazette, i.e., a slow technique from which the 1st solvent is extracted by the 2nd solvent just behind spinning at parenchyma.

[0012]In a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention, at least one or more melting peaks for which it asked by DSC need to exist in 140 ** - 148 **. As for especially it, in two or more peaks, it is preferred that it is a main peak with the biggest endothermic value. It is thought that a main peak reflects average structure (EC) of occupying a main part of textiles, and it becomes less enough [less than 140 ** / the heat resistance of the textiles themselves] as. moreover -- if it exceeds 148 ** -- the average fiber structure -- rather -- binding force -- it is high -- for example, it is extended, and becomes in end chain structure, and the fatigability of the textiles themselves falls rather. This invention persons reached obtaining the fatigue characteristics of textiles, and textiles which find out becoming optimum when the bending fatigue characteristic has this main peak in 140 ** - 148 ** in this case especially, and are used for highly efficient polyethylene which is this invention.

[0013]A high intensity polyethylene fiber used for a highly efficient fishing line which is this invention on the other hand needs existence of at least one peak for not less than 148 **. That is, I think that it corresponds with HMC structure where the 2nd melting peak (T_{m2}) that exists in not less than 148 ** in two or more endothermic peaks which can be set to DSC measurement of textiles concerning this invention influences an important antiwear characteristic greatly in the fatigue-resistant characteristic, especially this invention. As for textiles which do not have a peak at not less than 148 **, an antiwear characteristic gets extremely bad although a mechanism of the formation will be described later.

[0014]thus, as compared with the conventional high intensity polyethylene fiber, fatigue characteristics, especially abrasion characteristics-proof of a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention were

boiled markedly, and have improved. Specifically in an attrition test measured based on the JIS B method (JIS L1095), the number of times of cutting of textiles serves as 100,000 times or more of high intensity polyethylene fibers.

[0015]Although a method of manufacturing a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention recommends a method which needs to adopt a prudent and new manufacturing method and is indicated below, of course, it is not limited to it. That is, as for limiting viscosity [eta] of polyethylene of the amount of Polymer Division which serves as the raw material in manufacture of the textiles concerned, it is important that it is five or more, and it is ten or more still more preferably eight or more preferably. High intensity textiles of 22 or more cN/dtex are not obtained for mean intensity of textiles originally carried out to limiting viscosity being less than five with a request. On the other hand, as for limiting viscosity of polymer which serves as a raw material from a viewpoint of fatigue-characteristics-proof grant, although it is infinite to limiting viscosity like the above, 2.9 or less are preferred.

[0016]in a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention -- the main ingredients of polymer -- an ethylene ingredient -- more than 99.5mol% -- it is preferably important that it is a homopolymer of polyethylene substantially beyond 99.8mol%. Although recommended rather, introduction of branching of a **** small quantity for the purpose of improving the creep property etc. of textiles obtained by making a side reaction and a rate of polymerization of a polymerization improving is not preferred to the fatigue characteristics of textiles, if copolymer components, such as an alpha olefin, increase too much. It is presumed whether although it is not certain, if copolymerization of a small amount of alpha olefins is carried out, a slide between chains within a crystal will be controlled, and this cause inhibits an operation which this makes ease stress to modification of a continuous repetition (it misses).

[0017]In a manufacturing method which a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention recommends, The uniform dissolution can be performed for polyethylene of such an amount of Polymer Division using nonvolatile solvents, such as volatile solvents, such as a decalin tetralin, paraffin, solid paraffin, and a dope for spinning can be obtained. Under the present circumstances, concentration is preferably [2.9% or less of] desirable 50% or less. As for a solution used, if it furthermore says, it is preferred that it is a volatile solvent. Speed which extracts a solvent out of thread in an ordinary temperature solid or a non-volatile solvent is slow, and it is difficult to fully form HMC described by this

invention. It is presumed that this Reason becomes possible [forming a unique crystal structure (HMC) in which a surface solvent evaporates more positively, concentration is high and a chain carries out orientation more near the fiber surface in a stage of spinning and which chains connected by using a volatilization solvent]. In common sense of the conventional spinning art, a structure difference of such the surface and an inside becomes a factor which reduces intensity of textiles, choosing spinning conditions in order to use homogeneity of a cross sectioned direction as much as possible also sets dry spinning and wet spinning, such as not only gel spinning but polyvinyl alcohol, and polyacrylic nitril, to melt spinning from the first -- that is, spinning -- it was the common sense of the engineer concerned engaged generally.

[0018]This invention persons make structure of a inner layer and an outer layer change positively rather in a stage of spinning against this common sense, Although intensity and an elastic modulus were maintained by specifically eliminating a solvent of a surface layer positively momentarily, and forming a HMC layer by making spinning tension concentrate on a surface layer by that cause, textiles possessing an antiwear characteristic and the bending fatigue characteristic of having excelled extremely found out obtaining and getting, and reached this invention.

[0019]That is, I think that the 2nd melting peak (T_{m2}) that exists in not less than 148 ** in two or more endothermic peaks which can be set to DSC measurement of textiles concerning a high intensity polyethylene fiber used for a highly efficient fishing line which is this invention as mentioned above originates in this HMC at least. It found out that high intensity polyethylene which has the optimal fatigue characteristics-proof could specifically be provided by controlling quantity of this 2nd melting peak, and the above-mentioned hypothesis was reached.

[0020]Having the structure which a mutual molecule confounds more HMC which exists in this surface layer, and is hard to fibrillate is imagined. That is, that the first cause of fatigue by crookedness and wear of orientation textiles which make a high intensity polyethylene fiber representation is in fibrillation from a surface layer of textiles is a fact generally known. That textiles of this invention which has a more precise surface structure are excellent in the bending-fatigue-resistance characteristic or an antiwear characteristic presumes that it is based on such a situation.

[0021]However, in this HMC, a rate of occupying to a crystal structure of the whole is important. Namely, although the 1st existing endothermic peak (140 ** - 148 **) (T_{m1}) presumes that it originates in fusion of EC and the 2nd peak (T_{m2}) that exists in not less than 148 ** originates in HMC at least like the above-mentioned, a ratio of height

of the greatest endothermic peak in each temperature region -- 1.5:1.0 to 2.9:1.0 -- it is preferably important 2.0:1.0 to 2.9:1.0 and that it is 2.1:1.0 to 2.8:1.0 still more preferably. If a peak by the side of low temperature becomes low relatively from 1.5:1.0, it will mean that a molar fraction of HMC presumed that this forms a surface layer of textiles becomes large too much, and fatigue characteristics-proof will get worse rather. This is presumed because degradation like buckling fatigue is promoted because a surface layer hardens too much. Although a HMC chain with which a peak value by the side of an elevated temperature becomes small rather than 2.9:1.0 in the ratio decreases relatively on the other hand and it is convenient to a strength property etc., a highly efficient fishing line in which raw material performance of a high intensity polyethylene fiber in which fatigue characteristics-proof made into the purpose of this invention were improved was made to reflect efficiently cannot be satisfied.

[0022]Anyway, a highly efficient fishing line obtained by this invention, Have intensity and the elastic modulus the former and more than comparable, and, in addition, excel in crookedness-proof / wear fatigue characteristics, and. Although a principle is only presumption, **** is carried out for obtaining a function surface and a highly efficient fishing line epoch-making in respect of practical use by using a high intensity polyethylene fiber which is excellent in blade resistance and cut resistance by being characterized by a surface layer being more precise.

[0023]A technique recommended when manufacturing a high intensity polyethylene fiber used as raw material of this highly efficient fishing line is supplying hot inactive gas compulsorily to a regurgitation solution which came out directly under [cap] spinning, and evaporating a solvent of the surface of a line of thread positively. thereby -- the surface -- **** -- a thin HMC layer can be made to be able to form and a unique structure which a chain of the above-mentioned concept connected mutually can be made to appear by centralizing tension in spinning It is recommended that not less than 60 ** of temperature [not less than 80 ** of] of inactive gas in this case is not less than 100 ** less than 150 ** still more preferably preferably. Under the present circumstances, gas is not limited although using nitrogen gas from an economical viewpoint is recommended.

[0024]Thus, obtained textiles may extend several times, being heated again and making a remains solvent evaporate, and may perform multi stage story extension by a case. New textiles which have the above-mentioned extremely outstanding characteristic can be obtained without HMC structure of the surface once formed with spinning disappearing in latter extension.

[0025]Although a gestalt in particular of a fishing line by this invention is not asked, what acted as a braid of the above-mentioned high intensity polyethylene fiber, a thing which allotted these textiles to wadding and which carried out covering yarn, or a thing which made these textiles throwing can be recommended.

[0026]A measuring method and a measuring condition about weighted solidity of a high intensity polyethylene fiber which constitutes this highly efficient fishing line in this invention are explained below.

[0027](Intensity and elastic modulus) Intensity in this invention, and an elastic modulus, Using "tensilon" by a cage ene tick company, 200 mm (length between zippers) of sample length, It calculated and asked for an elastic modulus (cN/dtex) from 100% of extension speed a tangent which measures distortion-stress lines on condition of for /under 20 ** of ambient temperature, and 65% of relative humidity conditions, and gives the maximum inclination intensity (cN/dtex) and near the curved starting point for stress in the curved point of rupture. Each value used average value of 10 times of measured value.

[0028](Limiting viscosity) Limiting viscosity was determined from an interpolating point to the starting point of a straight line which measures specific viscosity of various diluted solutions with an Ubbelohde capillary viscometer in a 135 ** decalin, and is obtained by least mean square approximation of a plot to concentration of the viscosity. Measurement was faced, a sample was divided or cut for a sample to the length of about 5-mm length, 1wt% of an antioxidant (made by brand-name "reed NOx BHT" Yoshitomi Pharmaceutical Industries) was added to polymer, the stirring dissolution was carried out at 135 ** for 4 hours, and a measurement solution was adjusted.

[0029](Differential scanning calorimeter measurement) Differential scanning calorimeter measurement used "DSC7" by PerkinElmer, Inc.Carried out about 5-mg restoration enclosure of the sample (textiles) beforehand judged to 5 mm or less at aluminum bread, and made aluminum bread of same sky into a reference, and it was made to go up from a room temperature to 200 ** under inactive gas with 10 ** the heating rate for /, and asked for the endothermic peak. Carry out baseline amendment of an obtained curve and the number of not less than 140 ** melting peaks is counted, A peak with the largest amount of endothermics was made into the 1st melting peak in 140 ** - 148 **, it is in not less than 148 **, a peak with the largest amount of endothermics was made into the 2nd melting peak, and it asked for each temperature and peak height, and asked for a rate of a peak ratio by **(ing) the former by the latter. When a peak was hard to be distinguished by the shape of a shoulder, a peak ratio was

computed by having substituted height of absorption at 150 ** as the 2nd melting peak.

[0030](Abrasion resistant test of thread) The antiwear characteristic of this fishing line was measured by yarn doubling or a method which adjusts and is based on the JIS B method (JIS L1095) so that it might become an equivalent for 1500dtex if possible about textiles. A friction child carried out load at a both-way distance of 2.5 cm, and 110 angles by 115 speed/of 0.5g [d] /using hard steel of 0.9 mmphi, and less than 1000 times of those of n= 2 times of average value rounded off and adopted.

[0031]The antiwear characteristic of a fishing line by this invention performed what adjusted a high intensity polyethylene fiber by this invention to a braid with the following test method.

[0032]A testing machine improved a hexagonal-bars abrasion tester of a seat belt, has arranged ceramic GAIGO in a position of hexagonal bars, and used it as a testing machine. Therefore, about stroke length, an angle, etc., it is proportionate to JIS-D-4604 (1995). As shown in drawing 2, a sample is fixed to a ceramic guide, through and one side are fixed to a drum, and load is applied to another side. Load applies load by a ratio of 1 g/d to a denier value of wadding. After making a drum move reciprocately 1000 times, the visual judgment of the state of a sample was carried out. if completely changeless as evaluation of an abrasion proof examination -- O -- when becoming fluffy for a while, or ** and fuzz were intense, when cutting also partly, it was estimated as x.

[0033](Strength retention) A powerful measuring method is proportionate to JIS L 1013, and compared powerful retention by a sample before and behind an abrasion resistant test described by an upper paragraph.

[0034]Hereafter, although this invention is concretely explained with working example, this invention is not limited to these.

[0035]

[Example]Hereafter, this invention is explained with working example.

(Working example 1) Limiting viscosity dissolves the homopolymer of ultra high molecular weight polyethylene of 21.0 and molecular-weight-distribution index Mw/Mn=3.7 with the screw type kneading machine set as the temperature of 230 ** while distributing the mixture of 10wt% and decahydronaphthalene 90wt% of slurry form, 0.7 mm in diameter set as 170 ** was supplied to the cap which carries out a 400 hole owner by solitary-foramen discharge quantity 1.4 g/min with the lightweight pump. As it hits a line of thread uniformly as much as possible in the nitrogen gas adjusted to 100 ** at 1.2 m/second high speed in the slit shape gas supply orifice

installed directly under the nozzle, the decalin of the surface of textiles is evaporated positively, It cooled substantially in the airstream set as 30 ** immediately after [that], and when [this] taken over the speed for 75-m/by the Nelson-like roller installed in the nozzle lower stream, the solvent contained filar was falling to the abbreviation half of the original weight. Then, the obtained textiles were succeedingly extended by 4 times in the heating oven which was extended 4 times under 100 ** heating oven and which installed these textiles in 149 **. The fineness of total textiles which was able to obtain uniform textiles without fracturing on the way was 455dtex. The property value of the obtained textiles is shown in Table 1. The fishing line adjusted to 55.6dtexx4 braid using the textiles obtained next was created, and the wear test was presented. The result is shown in Table 2.

[0036](Working example 2) It was a satisfying value although the fall was looked at by endurance a little which the temperature of the heating-at-high-temperature style in working example 1 was 120 **, and the mean wind was carried out in 1.4 m/second, and also performed spinning by the same operation. What was used as the 111.1dtexx4 braid using the textiles obtained next was created, and the attrition test was presented. The result is shown in Table 2.

[0037](Working example 3) Limiting viscosity made viscosity of the solution 30%, using polymer of 12.1 and molecular-weight-distribution index Mw/Mn=5.4 as main-ingredients polymer in working example 1, and also spinning was carried out by the same operation. In the 2nd step of extension whose 3 times as many extensions were possible for 1 step stretching, 2.2 times were a limit. The result is shown in Table 1. The whole fineness was 1160dtex. Intensity fell a little. What was used as the 111.1dexx4 braid using the textiles obtained next was created, and the attrition test was presented. The result is shown in Table 2.

[0038](Working example 4) The covering thread which used as wadding (880dtex) and volume thread (220dtex) the textiles which consist of high strength polyethylene of working example 1 was created, the abrasiveness examination of Table 2 was done, and the attrition test was presented. The result is shown in Table 2.

[0039](Working example 5) What made the textiles (1320dtex) which consist of high strength polyethylene of working example 1 throwing (number of twist 100 t/m) was created, the abrasiveness examination of Table 2 was done, and the attrition test was presented. The result is shown in Table 2.

[0040](Comparative example 1) In the experiment of working example 1, grant of the hot wind in the gas slit directly under a nozzle was stopped, and it cooled with 30 ** nitrogen gas promptly. The 2nd step fell [draw magnification] a little by a part for

75-m/, only low magnification was obtained, i.e., 1 step stretching was 4.0 times and 2 step stretching of spinning was 3.5 times. The physical properties of the obtained textiles are shown in Table 1. A DSC result is shown in drawing 4. Although the textiles which are equal to working example 1 mostly in intensity and elastic modulus were obtained, it was inferior to abrasion resistance, and thermal character was not satisfied, either, i.e., the peak by the side of an elevated temperature became in shoulder, and a clear peak was not acquired. Inside ** also substituted 140 ** - 148 ** for the peak value of 145.5 **, and the amount of endothermics in 150 ** by acquiring a peak at the 1st endothermic and the 2nd endothermic peak, respectively, and the ratio was computed by reference. What was adjusted to the 55.6dtexx4 braid using the textiles obtained next was created, and the attrition test was presented. The result is shown in Table 2.

[0041](Comparative example 2) After dissolving polymer of working example 1 with a liquid paraffin, unextended spinning thread was obtained on the same operation and spinning conditions. However, 4 times as many extensions were performed, carrying out real extraction of the solvent all over the bus of n-Deccan set as about 80 ** arranged under Nz of spinning. Cooling with the positive gas in an air gap was not carried out. The half-full oriented yarn including obtained n-Deccan was extended 4 times at 148 ** among the oven of hot inactive gas, real desiccation of the 2nd solvent was carried out, and the full oriented yarn was obtained. The physical properties of textiles are shown in Table 1. Although the textiles which are equal to working example 1 mostly in intensity and elastic modulus this time also were obtained, DSC is completely a single peak and the small shoulder was rather observed near 133 **. The antiwear characteristic of the obtained textiles was very a low. What was adjusted to the 55.6dtexx4 braid using the textiles obtained next was created, and the attrition test was presented. The result is shown in Table 2.

[0042]

[Table 1]

実験	[η] (g/dl)	繊度 (dtex)	強度 (cN/dtex)	弾性率 (cN/dtex)	摩耗試験回数	融解ピークの数	第1吸熱ピーク温度	第2吸熱ピーク温度	ピークの高さの比
実施例1	18.5	455	38.1	1521	421,000	3	142.0	148.5	2.4:1
実施例2	18.4	448	35.2	1612	356,000	2	144.7	151.3	2.4:1
実施例4	9.4	1150	28.5	1055	381,000	2	144.3	151.7	2.0:1
比較例1	18.4	541	34.2	1516	98,000	2	145.5	明確で無い	(3.2:1)
比較例2	18.3	471	35.7	1623	57,000	1	145.5	観測できず	—

[0043]

[Table 2]

実験	繊度 (dtex)	強度 (cN/dtex)	破断強力 (kg)	弾性率 (cN/dtex)	摩耗試験	
					1000回	強力保持率(%)
実施例1	222.6	23.8	4.9	594.7	形状変化なし	89.8
実施例2	503.4	23.3	9.5	583.2	形状変化なし	90.2
実施例3	550.1	26.8	12.9：	599.7	形状変化なし	84.5
実施例4	1110.1	25.4	24.9	409.8	形状変化なし	82.9
実施例5	1450.2	28.5	38.7	945.3	形状変化なし	80.6

[0044]

[Effect of the Invention]It made it possible to provide the highly efficient fishing line by the new high intensity polyethylene use which is excellent in the abrasion proof and fatigue characteristics which have high intensity and a rate of high elasticity, are equal to the general-purpose textiles for garments thread, or were excellent.